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On the conduction mechanism in granular materials

I. P. Zvyagin† and R. Keiper‡
† Faculty of Physics, Moscow State University, 119899 Moscow, Russia
‡ Institute of Physics, Humboldt University Berlin, 10115 Berlin, Germany

Abstract. We discuss the effect of virtual intermediate localized states on inter-grain tunneling that controls conduction in granular conductors on the insulating side of the metal–insulator transition. It is shown that intermediate states can substantially increase inter-grain tunneling transition probabilities and give rise to the conductivity temperature dependence of the form $\ln\sigma \sim -(T_0/T)^x$, where $x \approx 0.4$, and to a large enhancement of the conductivity.

Introduction

Granular conductors are finely divided mixtures of a conducting and nonconducting phases; granular metals with characteristic grain sizes in the nanometer range are most commonly studied. It has been established a long time ago that on the insulating side of the metal-insulator transition, the conductivity of many of these materials in a wide temperature range is small and is well described by

$$\sigma \sim \exp\{-(T_0/T)\}^x, \tag{1}$$

where T_0 is a parameter and the exponent is $x < 1$ (usually $x \approx 0.5$) (see [1–3]). Such behavior was observed in cermets, discontinuous metal films, granular Fe-SiO_2 films, heavily doped and organic semiconductors and other materials.

Numerous theories were proposed to explain the dependence (1). Practically all theories agree that the conduction mechanism in granular metals in the dielectric regime is activated tunneling (hopping) between grains with disorder in grain size and inter-grain separation. If hopping is restricted to near neighbors only [4–6], the conductivity temperature dependence (1) can be obtained if there exists some special structural correlation between the grain size d and inter-grain separation w, e.g., $w/d = const$ [4]. The analysis of Adkins [7] showed that there is no clear correlation between d and w; the implication is that variable-range hopping must be taking place. For an almost constant density of states, the standard argument gives the Mott law with $x = 1/4$ at low temperatures. Assuming for granular metals the quadratic Coulomb gap at the Fermi level [8], one obtains Eq. (1) corresponding to the Efros–Shklovskii law [9] often observed in doped semiconductors at low temperatures.

It was noted however that there are substantial difficulties in explaining the available experimental data by using the Coulomb gap model. The data for different types of granular metal systems were analyzed in [3] using this model. The estimated hop distance appeared to be too small for variable-range hopping to be effective. Moreover, fitting of magnitude of the measured conductivity required much lower values of α than those expected on the basis of the known electronic structure of the materials. In [8], the authors have attempted to improve the theory replacing the wave function decay parameter α by the effective parameter $\alpha_m \approx \alpha w/(w+d)$, where w is the average thickness of the insulating layer between adjoining grains and d is the grain diameter. This *ad hoc* assumption was not consistently justified but even with the use of this assumption, the explanation of

the observed temperature variation of the conductivity still appears to be difficult [3, 7]. Moreover, under typical experimental conditions the Coulomb gap effects are not expected to be important for granular metals. Indeed, the interaction is appreciably reduced by screening, the estimated hop distances are not large and the temperatures at which the dependence (1) is observed are too high. Accordingly, in what follows we do not consider inter-site correlations that produce the Coulomb gap. We discuss a different approach to the theory of conduction in granular metals related to the role of intermediate virtual states.

1. Effect of virtual states on distant-neighbor transition rates

In accordance with the standard approach, we assume that the conduction mechanism is inelastic tunneling (hopping) between states localized at different grains. The intergrain transition probabilities depend on the overlap of wave functions of different grains and hence on the edge-to-edge separation between the grains; for near grains it can be much smaller than the grain size. So we have a system with hopping sites of extended size; an example of such systems is a superlattice with intentional disorder. It was shown [10, 11] that when calculating distant-site transition rates, important contributions to transition rates can come from transitions involving intermediate virtual states. In what follows we demonstrate that virtual states also play an important role for distant-neighbor transitions in granular conductors.

For phonon-assisted single-electron transitions, the matrix element for phonon-assisted transitions between a given grain and a grain lying in the n th coordination sphere is expressed as a sum over different paths involving $n-1$ virtual intermediate states ($n-1$ steps corresponding to coherent tunneling and one step with phonon absorption or emission). In analogy with [11] it can be shown that the contribution of direct inelastic tunneling between distant initial and final grains can be neglected compared to the process involving virtual states; the ratio of the corresponding contributions to the transition rate is of the order of $(\Delta E/t_0)^{2(n-1)} \exp\{-2\alpha_0(w_{ab} - n\bar{w})\}$, ΔE is a characteristic energy difference of the levels of neighboring grains, t_0 is the preexponential factor in the transfer integral, w_{ab} is the edge-to-edge separation between the initial and final grains and $\bar{w}$ is the average separation between the near grains. For large grains and narrow inter-grain barriers, we have $w_{ab} >> n\bar{w}$ and this ratio is small due to the exponential gain in tunneling distance.

2. Percolation arguments

As in the standard hopping theory, the conductivity problem can be reduced to finding the resistance of the equivalent random network, where the sites correspond to grains and the conductances connecting sites i and j can be written as $G_{ij} = G_0 \exp(-2\alpha S_{ij} - E_{ij}/kT)$, where G_0 is the preexponential factor that only weakly (nonexponentially) depends on inter-site separations and grain energy levels, S_{ij} is the total tunneling distance, $S_{ij} = n\bar{w}$, $E_{ij} = |E_i - \mu| + |E_j - \mu| + |E_i - E_j|$ and E_i are effective one-particle energy levels introduced in a way similar to that used in the theory of multivalent defects in semiconductors [12]. Here the difference from the standard expression for inter-grain conductance is that due to large grain size, for distant grains i and j we have $S_{ij} < w_{ij}$.

If the scatter in transition rates is large, then we can apply the standard percolative arguments. We say that for some fixed $G = G_0 \exp(-\eta)$, any two sites i and j are bonded if $G_{ij} > G$, i.e., if $2\alpha S_{ij} + E_{ij}/kT < \eta$. The critical value of η corresponding to the percolation threshold can be estimated by the bonding criterion [13] stating that the threshold corresponds to the condition that the average number of bonds per site $\bar{\nu}$ attains some critical value ν_c.

To estimate the number of bonds, we must know the distribution of energy levels E_i of localized states in the energy domain near the Fermi level taking account of both confinement and Coulomb interaction effects. Due to weak overlap of localized wave functions of different grains, to a good approximation we can assume that the level positions for different sites are uncorrelated (see [14]).

The one-electron energy spectrum can be exactly calculated for an ideal spherical quantum dot in the absence of intra-site correlations [16]. Both the average interlevel distance and the average level degeneracy increase with energy; random fluctuations in grain shape as well as variations of work function for different crystallographic faces lift the level degeneracy [15, 14]. If the characteristic level splitting is larger than the level spacing for a spherical dot at the Fermi level, then in the relevant energy range the level distribution is practically uniform, and the effective density of states (per grain) for conductivity $\bar{\rho}_0$ is practically constant in the region of interest near the Fermi level. In this case the average number of bonds per site is easily evaluated.

In the continuous limit, for distant coordination spheres, we have for the average number of bonds per site $\nu = \int d\varepsilon \mathbf{dR} \rho_0 \theta\,(\eta - 2\alpha n(R)\bar{s} - \varepsilon/kT)$, where $\mathbf{R}$ is the position vector of the final grain, $\rho_0 = (r/v_0)\bar{\rho}_0$, r is the volume fraction of metal, v_0 is the average grain volume and $n(R)$ is the number of the coordination sphere. Due to large grain size, in granular metals there is strong correlation in spatial positions of the grains preserving a short-range order in the spatial arrangement of grains. So to find the function $n(R)$ of the dependence of the radius R_n of the n th coordination sphere on n, we can use a model of regular close packed structures. For a regular close packings of spheres (f.c.c. and b.c.c. structures), the variation of R_n versus n th is quite well approximated by $R_n \approx d \cdot n^{\beta}$, where $\beta \approx 0.5$. Using this, we can evaluate the integral in the expression for ν; then by the bonding criterion, we obtain for the conductivity Eq. (1), where $x = 1/(1 + 3\beta)$ and

$$T_0 = (B/k)\frac{(2\alpha\bar{s})^{3\beta}}{\rho_0 d^3}. \tag{2}$$

Here $B = 15\nu_c/16\pi$ is a constant; setting $\nu_c = 1.5$ (see [9]), we obtain $B \approx 0.45$.

3. Discussion

For $\beta = 0.5$ we have $x = 0.4$, i.e. we obtain the conductivity variation of the form (1) that is close to that usually observed experimentally.

By Eq. (2), we can estimate the values of material parameters. The data for a Ni-SiO_2 film with $r = 0.24$ produced by cosputtering [1] can be approximated by Eq. (1) with $T_0 = 6 \cdot 10^4$ K. The value of $\bar{\rho}$ is related to the characteristic interlevel spacing $\Delta = 1/\bar{\rho}$. Taking $\Delta = 50$ meV [14], from (2) we derive $2\alpha\bar{s} = 5$. For the estimated barrier width $\bar{s} = 0,7$ nm, we have the decay length of about 3 Å, which is reasonable.

Thus virtual states give rise to a substantial increase in inter-grain transition probabilities and to a temperature dependence of the conductivity of the form (1), where $x \approx 0.4$. It should be noted that this dependence is obtained for a model of variable-range hopping in the absence of Coulomb gap effects and with no appreciable energy disorder.

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